

PRODUCT YIELD AND HYDROGEN CONSUMPTION SELECTIVITY
TESTS FOR COAL LIQUEFACTION CATALYST DEVELOPMENT*

H. P. Stephens

Sandia National Laboratories, Albuquerque, New Mexico 87185

INTRODUCTION

Because hydrogenation of coal to liquid products (oils) is accompanied by distributions of complex by-product mixtures (IOM, preasphaltenes, asphaltenes and gases) which change as a function of reaction variables (time, temperature and pressure) and reactor configuration, the determination of selectivity relationships for coal liquefaction catalysts has been a difficult and time-consuming task involving numerous experiments to adequately describe catalyst performance over a range of conditions. This paper describes a method for analyzing the experimental results of coal liquefaction reactions which may be applied to a number of aspects of coal liquefaction research and process control, including: rapid selectivity and performance screening for catalysts; correlation of laboratory results with process parameters; and optimization of product yield for plant process conditions. Catalyst selectivity and performance screening will be emphasized here.

A primary goal of catalyst development for direct coal liquefaction is to maximize the yield of distillate products while minimizing the conversion to by-product hydrocarbon gases which unprofitably consume much of the hydrogen. Selectivity relationships for direct coal liquefaction catalysts have been difficult to determine and accurately describe, not only because of the complexity of the reaction mixtures, but also because of the difficulty of comparing the results of experiments performed at different times and temperatures or with different types of reactors. Imprecision in control of experimental variables such as temperature and contact time often causes significant differences in conversions for experiments for which the mean variables were designed to be nominally the same. Thus selectivity comparisons based on conversions at constant time and temperature are not entirely reliable.

The approach to selectivity relationships described in this paper is based on 1) a ternary product distribution diagram with a hyperbolic relation

$$y = \frac{x(c-x)}{a+bx} \quad 1)$$

between product and by-product conversions and 2) a hydrogen consumption diagram which relates the product conversion to the fraction of hydrogen consumed by the production of hydrocarbon gases. Each of these diagrams correlates, on a single curve, product distributions from reactions carried out over a wide range of experimental parameters, including temperature, time and different reactors.

Waterman first used ternary product distribution diagrams with reaction paths represented by

$$y = \frac{x(1-x)}{a+bx} \quad 2)$$

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to describe the catalytic hydroisomerization of paraffin wax (1) and later demonstrated their application to the characterization of many other complex chemical processes (2). Although the technique has been used to describe other hydrogenation processes (2,3), application to direct coal liquefaction has been unexplored. The results and analysis of direct coal liquefaction experiments described in this paper demonstrate the general applicability of ternary and hydrogen consumption diagrams to selectivity tests for coal liquefaction catalyst development.

EXPERIMENTAL

Materials

Liquefaction reactions were performed with Illinois No. 6 coal, SRC-II heavy distillate from the Ft. Lewis pilot plant (1:2 coal:solvent, by weight) and high purity hydrogen. An extensively used commercial HDS catalyst, American Cyanamid 1442A, an alumina supported CoMo formulation, was tested to establish base-line selectivity relationships. The catalyst extrudates were ground to a -200 mesh powder and added to the reaction feed slurry on a 5 weight percent coal basis. This quantity of CoMo/alumina was equivalent to 0.15% Co and 0.45% Mo. To test the utility of the selectivity relationships, additional microreactor experiments were performed with 0.3% Mo as molybdenum naphthenate (6% solution of molybdenum in naphthenic acid, obtained from Research Organic/Research Inorganic, Inc.), along with a control experiment with the equivalent amount of naphthenic acid alone.

Apparatus and Procedure

Two types of reactor systems were utilized, 30 cm³ batch microreactors (4), and a one-liter autoclave (5). For the low to moderate conversion range, microreactor experiments were performed at 1000 psig cold charge hydrogen pressure and over a wide range of times, $t = 0.5$ to 80 min, and temperatures, $T = 350^\circ$ to 425°C . Two autoclave experiments were conducted at 1000 psig and 425°C for 30 and 120 min to obtain data for high conversions. Temperatures and pressures were accurately recorded during the course of each experiment. Following the heating period of each experiment, the reaction vessel was quenched to ambient temperature, the resulting pressure was recorded, a gas sample was taken, and the product slurry was quantitatively transferred to a flask and subsampled for analysis.

Product Analysis

Gas samples were analyzed for mole percentages of CO, CO₂, H₂S and C₁-C₄ hydrocarbons with a Hewlett-Packard 5710A gas chromatograph, which was calibrated with standard mixtures of hydrocarbon gases and H₂S in hydrogen, obtained from Matheson Gas Products. Hydrogen in the samples was obtained by difference as the remainder of the product gas mixture. The quantity of each gas produced was calculated from the mole percent in the gas sample and the post-reaction vessel temperature T and pressure P using an ideal gas law calculation:

$$n_i = \frac{PV}{RT} f_i \quad 3)$$

$$w_i = FW_i n_i \quad 4)$$

where n_i = number of moles of component i
 f_i = mole fraction of i in the gas sample = mole %/100
 V = gas volume of reactor
 w_i = weight of i
 FW_i = the formula weight of i

Hydrogen consumed during the reaction was obtained as the difference between the initial charge and hydrogen remaining after the reactor was quenched.

The reaction product slurry was analyzed for insols, preasphaltenes, asphaltenes, and oils by tetrahydrofuran (THF) solubility and high performance liquid chromatography (HPLC). A 0.2 gm subsample was mixed with about 50 ml of THF, filtered to obtain the weight of insols, and brought to 100 ml with additional THF. Chromatograms of 5 μ l aliquots of the filtrate were obtained with a Waters Assoc. Model 6000A solvent delivery system equipped with a Model 440 uv absorbance detector. Separations of the solution into three fractions, preasphaltenes, asphaltenes, and oils, were effected on 100 A micro-syrage gel permeation columns. The uv absorbance response factors for the product separations were determined using standards prepared by dissolving known amounts of preasphaltenes, asphaltenes and oils obtained by soxhlet separation of whole liquid product from preparatory liquefaction experiments (6). Peak height measurement and response factors were used to calculate the percentages of preasphaltenes, asphaltenes and oils for the THF soluble product. All yield and conversion data were calculated on a dry mineral matter-free (dmmf) coal basis, which included a correction for the conversion of pyrite content of the coal to pyrrhotite.

RESULTS AND DISCUSSION

Process Course and Selectivity

Two ternary diagrams of product/by-product distributions for the coal liquefaction experiments previously described are shown in Figures 1 and 2. Conversion data for the various experiments are represented by the following symbols-- \bullet Co/Mo catalyzed; \blacksquare Mo-naphthenate catalyzed; and \square naphthenic acid blank. In Figure 1, asphaltene conversion is plotted against oil conversion (both wt % dmmf basis) and in Figure 2, the sum of mole percent oil and asphaltene conversion is plotted vs mole percent hydrocarbon gas conversion. Because of the large difference between molecular weight of gases (CH_4 to C_4H_{10} -- 16-58) and other products (e.g., oils--200 to 400), the mole percent basis is used to more precisely represent the ternary diagrams involving hydrocarbon gases. For the purpose of calculating mole percentages, average molecular weights of 2400, 1200, 600 and 300 were assumed for the fractions of IOM, preasphaltenes, asphaltenes and oils. These values approximately correspond to the middle of the molecular weight distribution ranges for these fractions (7). Moles of gases produced were experimentally determined as previously described.

Figures 1 and 2 illustrate several general observations which can be made about the coal liquefaction process. First, although the liquefaction process is complex, involving myriad chemical species, its course can be quantitatively described by simple diagrams relating groups of compounds which react in similar and predictable manners.

These diagrams may roughly be considered the kinetic analog of equilibrium phase diagrams in which the number of components of a system is the smallest number of independently variable constituents. The composition of the liquefaction reaction mixture is given by the fractions explicitly represented by the x and y axes, and a remainder portion represented by the length of a horizontal tie line from a point on the curve to the diagonal axis connecting the x and y axes. For Figure 1, asphaltene and oil conversion are given by the y and x axis and preasphaltene, IOM and gases by the tie line. Second, the hyperbolic relationships for the conversion of the fractions shown in the figures represent unique reaction paths for the Co/Mo catalyzed reactions, over a wide range of operating conditions--time, temperature and reactor type. Deviations from this hyperbola represent conditions which change the process course, for example, the onset of competing pyrolysis reactions at high temperatures which form coke and gas. This indicates that the selectivity for a coal liquefaction catalyst, with respect to product groups, may be uniquely described by hyperbolic relationships. Support for this hypothesis is given by the analysis of the selectivity for a set of two unidirectional, consecutive reactions for which the selectivity may be described by relative concentrations given by hyperbolic equations of one constant (2, 8).

The utility of ternary diagrams and hyperbolic relationships exemplified by Figures 1 and 2 is that they may be used to rapidly screen for catalyst selectivity. Once hyperbolic relations are derived for a baseline catalyst, the selectivity of another catalyst may be screened by comparison of its product/by-product distributions for one or two experiments with the hyperbola of the baseline catalyst. It can be seen in Figure 1 that the point for the Mo naphthenate experiment falls below the curve for Co/Mo but above the blank experiment. This indicates that the order of asphaltene to oil selectivity is:

$$\text{Blank} < \text{Mo-naphthenate} < \text{Co/Mo}.$$

In Figure 2, the sum of the coal conversion products, oils and asphaltenes, are plotted as a function of unwanted by-product hydrocarbon gas conversion. Again, the Mo-naphthenate point falls between the Co/Mo curve and the blank. Thus Mo-naphthenate, at the concentration used is not as selective for asphaltene and oil conversion as Co/Mo, but does promote a better product/by-product ratio than the non-catalyzed experiment.

Hydrogen Consumption Diagram

Another useful relationship developed to determine the efficiency or selectivity of a hydrogenation catalyst with respect to process hydrogen consumption is illustrated in Figure 3, a plot of the sum of oil and asphaltene conversion (wt %, dmmf) as a function of the fraction of hydrogen consumed by production of hydrocarbon gases (the ratio of the weight of hydrogen in the hydrocarbon gases to the hydrogen consumed). Again, a wide range of experimental conditions for hydrogenation of coal catalyzed by Co/Mo can be represented by a single curve. This diagram provides a more significant selectivity test than the hyperbolic correlations in that it relates directly to a primary goal of catalyst development for direct coal liquefaction--maximizing the yield of distillate products with respect to hydrogen consumption. Figure 3 illustrates that hydrogenation efficiency of Co/Mo-catalyzed conversion of coal to oil and asphaltenes sharply

decreases above conversions of about 80%. Points representing experiments for other catalysts falling below the Co/Mo curve indicate that these catalysts are less efficient than Co/Mo with respect to hydrogen consumption. The point representing the Mo-naphthenate experiment falls close to the Co/Mo curve indicating an efficiency nearly equal to Co/Mo, while the blank experiment (naphthenic acid) shows that non-catalyzed coal conversion is much less efficient in hydrogen consumption.

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Key to Figures

| Number | Symbol | Reactor | Catalyst | T(°C) | t(min) |
|--------|--------|-----------|-----------|-------|--------|
| 1 | ● | Micro | Co/Mo | 350 | 15 |
| 2 | ● | " | " | 375 | 15 |
| 3 | ● | " | " | 425 | 0.5 |
| 4 | ● | " | " | 400 | 15 |
| 5 | ● | " | " | 425 | 10 |
| 6 | ● | " | " | 425 | 15 |
| 7 | ● | " | " | 425 | 40 |
| 8 | ● | " | " | 425 | 80 |
| 9 | ● | Autoclave | " | 425 | 30 |
| 10 | ● | " | " | 425 | 120 |
| 11 | ■ | Micro | Mo-Naphth | 425 | 30 |
| 12 | □ | " | Blank | 425 | 30 |

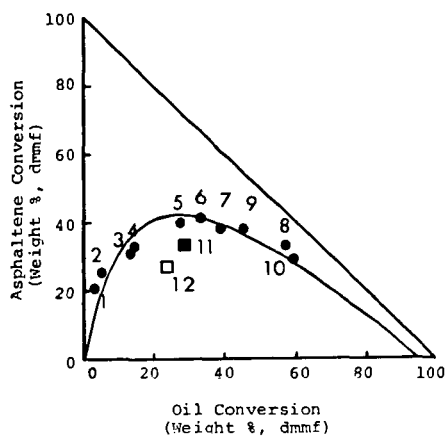


Figure 1. Ternary diagram of asphaltene vs. oil conversion. The curve, given by the equation

$$y = \frac{x(95-x)}{16.9+1.00x}$$

represents the process course for the Co/Mo catalyzed experiments.

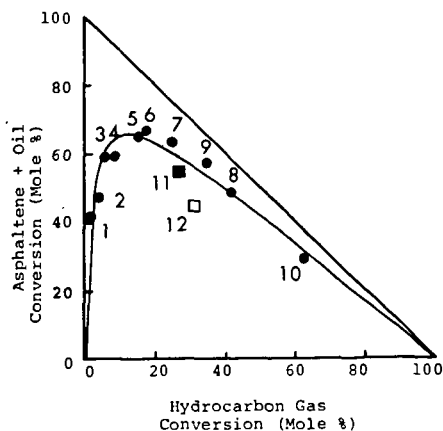


Figure 2. Ternary diagram of the sum of asphaltene and oil conversion vs. hydrocarbon gas conversion. The curve is given by the equation

$$y = \frac{x(100-x)}{2.35+1.15x}$$

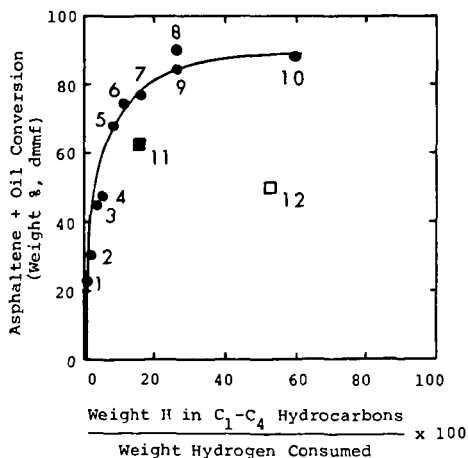


Figure 3. Hydrogen consumption diagram for direct coal liquefaction experiments. Curve represents Co/Mo catalyzed experiments.